GRAPEFRUIT SEED OIL
Manufacture and Physical Properties

by
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The commercial preparation of grapefruit seed oil as practiced in Florida is described, and physical characteristics of the crude oil obtained are given. The crude oil has an extremely bitter taste which is probably due to limonin ($C_{26}H_{30}O_8$). The oil can be easily refined, and the refined oil has a bland taste. Physical characteristics of refined and "wintered" refined oils are given.

Commercial production of grapefruit seed oil is a new industry in Florida. The seeds are readily collected from canneries where they are separated during the process of canning grapefruit juice and sections. During the 1938-39 season in Florida, canneries used approximately 8,298,454 boxes (about 331,938 tons) of seeded varieties of grapefruit. The average yield of seeds from seeded varieties in Florida amounts to about 4.7 per cent, based on the weight of the whole fruit. On this basis the potential yield of wet seeds during the 1938-39 season amounted to 15,601 tons from which 3,932,000 pounds of crude oil could be obtained theoretically. (Air-dried seeds contain 28-35 percent oil. The figures given are based on 30 percent oil content.) As a matter of fact, 90,000 pounds of crude oil were produced, because not all seeds available were utilized.

The fresh seeds contain from 55 to 60 percent moisture; the hulls constitute about 23 percent of the air-dried seeds. The composition of the whole air-dried seeds and air-dried hulls is indicated in Table I.

Table I. Analysis of Whole Air-Dried Grapefruit Seeds and Air-Dried Hulls

Seeds		Hulls	
Moisture	11.86%	Moisture	10.19%
Crude fat (ether ext.)	30.30	Ash	2.97
Protein (N X 6.25)	15.94	Protein (N X 6.25)	4.00
Crude fiber	9.14	Crude fat (ether ext.)	1.17
Ash	2.48	Crude fiber	39.75
N-free ext.(by difference)	30.28	Cellulose (Cross & Bevan)	32.50
SiO_2	0.28	Pentosans	16.34
Fe + Al (Fe_2O_3 + Al_2O_3)	0.50		
Ca	0.36		
Phosphates (P_2O_5)	0.56		
Na	0.052		
K	0.54		

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Table II. Composition of the Press Cake Obtained in the Preparation of Grapefruit Seed Oil.

Moisture	3.43%	SiO_2	0.081%
Ash	4.04	S	0.088
N as NH_3	4.21	Ca	0.35
N as protein	21.60	Mg (MgO)	0.39
Crude fat (ether ext.)	13.95	NaCl + KCl	2.48
Crude fiber	26.50	Phosphates (P_2O_5)	0.55
		Fe	0.0014

Production of Oil

The seeds (containing from 55 to 60 percent moisture) are collected from the canneries and trucked to the oil plant, where they are dumped into a storage bin and then conveyed to a large tank partially filled with water. Here the seeds undergo fermentation and souring which loosen the slimy coating and adherring pulp. This usually requires from 24 to 48 hours and is accelerated somewhat by the addition of small amounts of phosphate. Tricalcium phosphate is generally used because of its cheapness. If the seeds remain too long in the tank they become putrid and yield a foulsmelling oil.

After the seeds have been soaked, they are drained on a screen and steamed. At this point the hulls have cracked and the seeds contain 40 to 45 percent moisture. They are dried in rotary dryers until the moisture content has been reduced to 2.5 or 3.0 percent. The dried seeds are stored in bins until ready to be conveyed to the expeller. The expressed oil is allowed to settle and is then pumped through a plate-and-frame press.

The press cake obtained is broken up, bagged, and sold either as fertilizer or as an adjunct to dehydrated cannery waste for cattle feed. Analysis of the cake (Table II) shows that the cake still contains appreciable amounts of oil. Other analyses have shown that in some instances the oil content may run as low as 8 percent and as high as 19 percent. Such a high residual oil content would lead one to doubt the feasibility of obtaining the oil by expression. It may be that solvent extraction would prove a better method. With the present technique about 10 tons of wet seeds yield 1 ton of a crude filtered oil.

Properties of Commercially Expressed Oil

The unrefined oil has a reddish-brown color in moderately thick layers, a pleasant nutlike aroma, and an intensely bitter taste. It becomes cloudy at about 15°C. (59°F.), pasty at 4°C. (39.2°F.), buttery at -4°C. (24.8°F.), and solid at -10°C. (14°F.).

Jamieson, Baughman, and Gertler (2) examined an experimental batch of expressed grapefruit seed oil, but at the time of their studies the oil was not being produced commercially. For this reason it was thought advisable to examine the oil as it was being produced commercially and to supplement the work of the above investigators. The physical characteristics of the crude commercial oil are shown in Table III.

Table III. Physical Characteristics of Unrefined Grapefruit Seed Oil

	Commercial Oil	Exptl. Oil (2)
Sp. gr., 25°/25° C.	0.9197	0.9170
Refractive Index, n^{25}_{D}	1.4698	1.4700
Acid value	0.95	2.5
Saponification value	193.0	194.1
Iodine number (Hanus)	100.9	106.3
Unsaponifiable matter, %	0.48	0.7
Acetyl value	2.4	7.7
Reichert Meissl value	0.47	.....
Potenski value	0.20	.....
Moisture and volatile matter, %	0.13	.....
Meal content, %	0.05	.....

Refining of Crude Oil

Refining tests were carried out according to the Official Methods of Chemical Analyses of the American Oil Chemists' Society, so far as the percentage and strength of lye were concerned. It was not possible, however, to use the exact apparatus specified by the society.

The maximum amount of sodium hydroxide allowable was calculated according to the formula:

$$\frac{\text{free fatty acids}}{4.365} + 0.77 = \text{max. NaOH}$$

The concentrations of sodium hydroxide recommended by the society for oils of 0.5 percent free fatty acids are 16° and 20° Be. Tests were run with the maximum amount of the stronger sodium hydroxide and 80 percent of the maximum of the two sodium hydroxide solutions as specified by the society. The method finally used was essentially as follows: A weighed amount of oil was placed in a beaker; the oil was warmed to 30°C. (86°F.), and the calculated amount of sodium hydroxide was added with slow constant stirring. The oil was then warmed to 43-49°C. (109.4 - 12.2°F.) until the oil emulsion broke. The break usually occurred in about 10 minutes. The foots were then allowed to settle; the oil was filtered on a Buchner funnel, and the foots were sucked as dry as possible.

Results of refining tests are shown in Table IV. Test 3 shows the least refining loss, and this was checked by a duplicate determination. A refining loss of 5.5 percent is 1.2 percent more than would be obtained in good refinery practice; the excessive loss may be attributed to the fact that the foots were not pressed because of the small size of the sample used. That more neutral oil could be recovered was proved by using the method proposed by Wesson (1), which consists of extracting a known quantity of crude oil in petroleum ether with 14 percent potassium hydroxide and alcohol. The ether solution is then washed with 50 percent alcohol to remove soap, and the ether subsequently removed by evaporation. The residue consists of neutral oil. The percentage obtained is multiplied by 96.5 percent to obtain the refinery recovery. By this method 99.3 percent of neutral oil was obtained which in-

dicates a refinery recovery of 95.8 percent.

The composition of foots obtained in refining is shown in the following table. The neutral oil content is high, owing to the fact that the foots were not pressed.

Moisture	33.34%
Neutral oil	33.70
Fatty acids from soap	22.44
Ash (as Na_2O)	7.08
Nonfatty material	3.4

Bleaching and Wintering of Refined Oil

After treatment with sodium hydroxide the oil no longer possessed a bitter taste. The oil was washed with warm water and then heated to 110°C. (230°F.) until moisture had been removed. Decolorizing carbon and a filtering aid (0.5 and 2 percent, respectively, based on the weight of the oil) were added, and the mixture was maintained at 110°C. for 15 minutes with gentle agitation. The oil was then filtered by means of vacuum. Amounts of decolorizing charcoal greater than 0.5 percent did not give a lighter colored oil.

The bleached oil was light straw in color in moderately thick layers, and possessed a bland taste and, when hot, a faint oily odor. Characteristics of the refined and bleached oil are given in Table V. Refining caused a decrease in specific gravity, refractive index, acid value and unsaponifiable matter, and an increase in saponification value; the iodine number was not significantly affected.

Refined and bleached oil was chilled to 1°C. (33.8°F.) and pressed at this temperature by a small hand press. Sufficient pressure could not be obtained to express all of the oil from the solidified stearin. This "wintered" oil was light yellow in color and had the characteristics shown in Table V.

Table IV - Refinery Tests on Crude Commercially Produced Grapefruit Seed Oil (500-Gram samples)

Test No.	% NaOH Added		Soap Stock, Grams	Neutral Oil, Grams	Refining Loss %
	16° Be	20° Be			
1	8.6	...	78	451	9.2
2	8.0	...	71	465	7.4
3	6.4	...	57	477	5.4
4	...	6.6	92	463	10.8
5	...	6.1	90	444	11.4
6	...	4.9	76	448	10.4

Table V-Physical Characteristics of Bleached and of Wintered Grapefruit Seed Oil

	Bleached	Wintered
Sp. gr., 25°/25°C.	0.9179	0.9199
Refractive index, n_D^{25}	1.4688	1.4700
Acid value	0.17	0.26
Saponification value	197.5	192.2
Iodine number (Hanus)	101.7	109.2
Unsaponifiable matter, %	0.38	....

Isolation of Bitter Principle from Crude Oil

The soap stock obtained in refining the crude oil was acidified with hydrochloric acid and extracted with benzene. To the benzene extract was added three times its volume of petroleum ether; the precipitate formed was filtered, washed with petroleum ether, and dissolved in glacial acetic acid from which it was allowed to crystallize. After recrystallization from acetic acid, it was boiled with water, filtered, and washed free from acid. The material thus obtained was recrystallized from a mixture of benzene and ethyl alcohol and dried for 16 hours at 105°C. (221°F.). The dried material consisted of plates melting at 285°C. (545°F.) and possessed an intensely bitter taste. Further recrystallization failed to change the melting point. Tests for phenol, higher ketones, nitrogen, halogens, and sulfur were negative. The material reduced Fehling solution at boiling temperature. The evidence seems to indicate that it is limonin which Bernay in 1841 found in the seeds of several varieties of citrus fruit (1).

Analysis: Calculated for $C_{26}H_{30}O_8$: C, 66.35; H, 6.43; O_2, 27.22; found: C, 65.46; H, 6.87; O_2, 27.67.

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Literature Cited

1. Bernay, Ann., 40, 317 (1841).
2. Jamieson, Baughman, and Gertler, Oil & Fat Industries, 7, No. 5, 181 (1930).

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